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Quebec***

***Guoxiang Chi and Denis Lavoie***

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# A combined fluid-inclusion and stable isotope study of Ordovician ophicalcite units from southern Quebec Appalachians, Quebec<sup>1</sup>

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**Abstract:** This paper reports on microthermometric data of fluid inclusions from calcite cements in ophicalcite units from the Rivière des Plantes ophiolitic mélange, and integrates them with previously published stable isotope data to estimate the isotopic composition of the parent fluids. Potential primary fluid inclusions may be either monophasic (liquid) or biphasic (liquid+vapor). The biphasic fluid inclusions show an overall range of homogenization temperatures ( $T_h$ ) from 85°C to 173°C, and final ice-melting temperature ( $T_{m-ice}$ ) from -6.6°C to -2.3°C. The monophasic fluid inclusions show  $T_{m-ice}$  values similar to those of the biphasic fluid inclusions, and possibly have been entrapped at temperatures around or lower than 50°C. The  $\delta^{18}O$  values of the parent fluids are estimated to be -1.9‰ to +4.9‰ SMOW if the biphasic inclusions are primary, and -7.8‰ to -6.6‰ SMOW or lower if the monophasic fluid inclusions are primary.

**Résumé :** Cette contribution présente des données sur les inclusions fluides présentes dans des ciments de calcite de la succession d'ophicalcite du mélange ophiolitique de la Rivière des Plantes et les intègre aux résultats d'études isotopiques déjà publiées afin d'estimer la composition en isotopes stables des fluides parents. Les inclusions fluides potentiellement primaires peuvent être soit monophasées (liquides) ou bien biphasées (liquide + vapeur). Les inclusions biphasées offrent un champ de température d'homogénéisation ( $T_h$ ) allant de 85 à 173 °C et une température finale de fonte de glace ( $T_{f-glace}$ ) variant de -6,6 à -2,3 °C. Les inclusions fluides monophasées montrent des valeurs de  $T_{f-glace}$  similaires à celles des inclusions fluides biphasées et ont été possiblement piégées à des températures proches de 50 °C ou inférieures. Les estimations des valeurs de  $\delta^{18}O$  des fluides parents se situent dans l'intervalle de -1,9 à +4,9 ‰ SMOW si les inclusions fluides biphasées sont primaires et dans celui de -7,8 à -6,6 ‰ SMOW, ou sont même inférieures, si les inclusions fluides monophasées sont primaires.

<sup>1</sup> Contribution to the Appalachian Foreland and St. Lawrence Platform Architectures in Quebec, New Brunswick and Newfoundland NATMAP Project

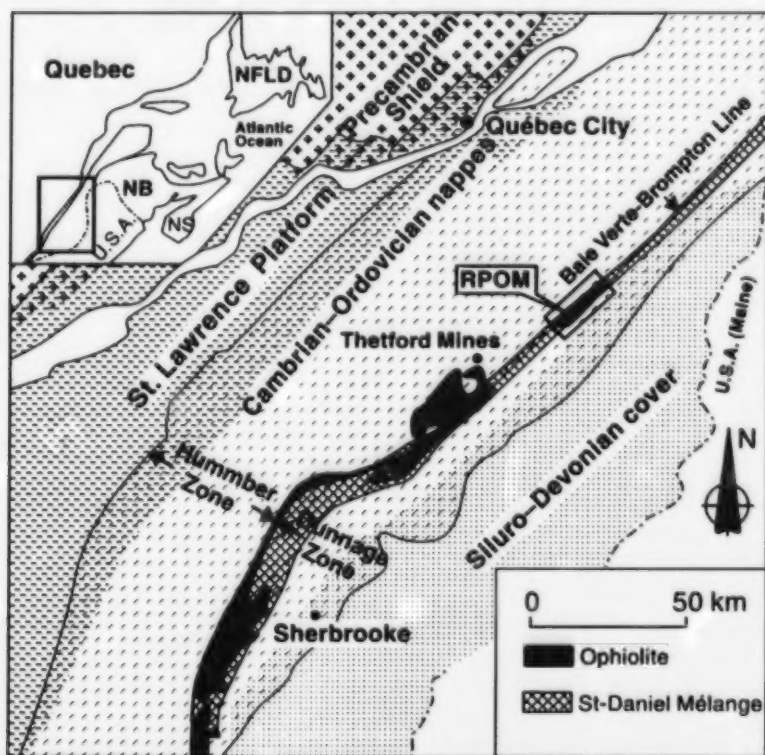
## INTRODUCTION

Ophicalcite units from the southern Quebec Appalachians have been studied previously for petrography and O and C isotopes (Lavoie and Cousineau, 1995; Lavoie, 1997). It was proposed that the ophicalcite units were formed in a seafloor hydrothermal vent system (Lavoie and Cousineau, 1995), and that the peloidal mats in the ophicalcite represent fossil analogues of bacterial white slime around modern vents (Lavoie, 1997). This paper reports on fluid-inclusion study of the same set of samples that were studied for O and C isotopes. Unlike ophicalcite units from the Alps which show significant oxygen isotope re-equilibration due to regional metamorphism (Weissert and Bernoulli, 1984; Früh-Green et al., 1990), the ophicalcite units from southern Quebec appear to have preserved the original oxygen isotopes (Lavoie and Cousineau, 1995). It is consequently inferred that fluid inclusions entrapped during precipitation of calcite may not have been subject to significant post-trapping alteration, and may provide information about the fluid composition and thermal condition in the formation of the ophicalcite.

## GEOLOGICAL SETTING AND SUMMARY ON PETROGRAPHY AND STABLE ISOTOPES

The ophicalcite units of this study were sampled from the Rivière des Plantes ophiolitic mélange, which is one of a series of ophiolitic complexes situated along the Baie Verte–Brompton Line in southern Quebec Appalachians (Fig. 1). The Baie Verte–Brompton Line is the surface expression of a suture zone between oceanic rocks of the Dunnage Zone and continental rocks of the Humber Zone (Williams and St-Julien, 1982). The Humber Zone consists of Cambrian–Ordovician slope, rise, and foredeep sediments of the Laurentian continental margin, whereas the Dunnage Zone comprises arc and back-arc volcanic rocks and fore-arc basin sediments, which were accreted to the Humber Zone when the Iapetus Ocean closed during the Ordovician Taconian Orogeny (Tremblay et al., 1995).

The Rivière des Plantes ophiolitic mélange is composed of diverse serpentinized ultramafic rocks, amphibolitized gabbro, basalt, granitoid, and metasandstone units. It occurs as a series of tectonic slivers piercing through the Early to Middle Ordovician Saint-Daniel mélange (Fig. 1). Ophicalcite units occur as a minor component within the



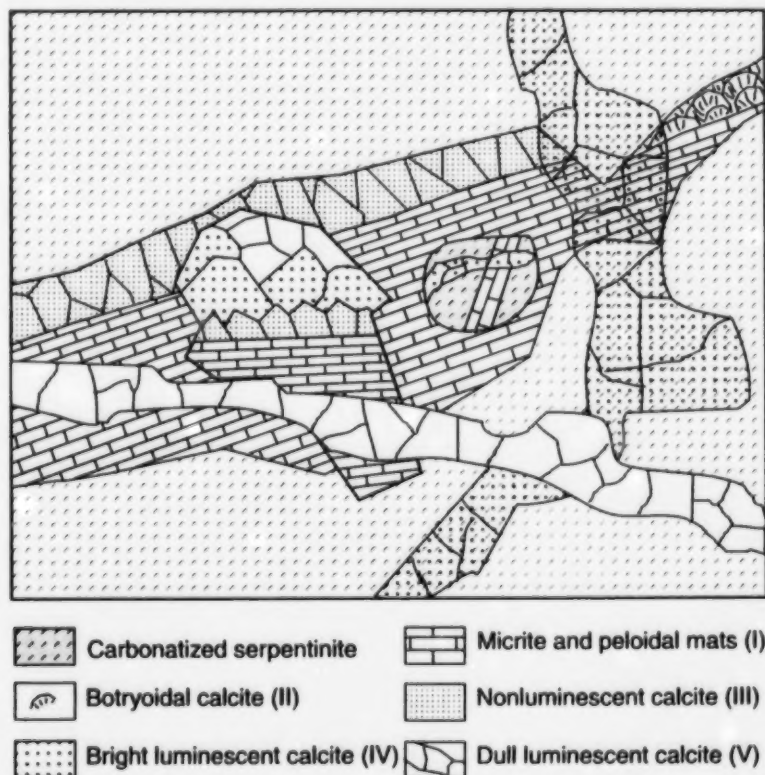
**Figure 1.** Location and geological setting of the ophicalcite units from southern Quebec Appalachians (modified from Lavoie and Cousineau, 1995). RPOM = Rivière des Plantes ophiolitic mélange.

ophiolitic complex, and consist of various calcite phases and serpentinized ultramafic blocks (Lavoie and Cousineau, 1995). The various components of the Saint-Daniel mélange, including the Rivière des Plantes ophiolitic mélange, were shown to have accreted to the Humber Zone from Middle to Late Ordovician, i.e. during the Taconian Orogeny (Cousineau and St-Julien, 1992). Although there is no direct evidence for the age of formation, the Rivière des Plantes ophiolitic mélange may have formed during Early to Middle Ordovician, prior to its emplacement in the Saint-Daniel mélange. The Rivière des Plantes ophiolitic mélange was affected by Taconian and Acadian (mid-Devonian) orogenies, and was metamorphosed to lower greenschist facies.

The samples used in this study have been examined for petrography in previous studies (Lavoie and Cousineau, 1995; Lavoie, 1997). The salient petrographic features are summarized here in order to provide a basis for description and discussion of fluid-inclusion and stable-isotope data in the following sections. Five types of calcite have been distinguished, including I) sedimentary calcite (mostly micrite and peloidal mats), and (II–V) pore- and fracture-filling calcite; II) dull-luminescent, botryoidal calcite; III) nonluminescent,

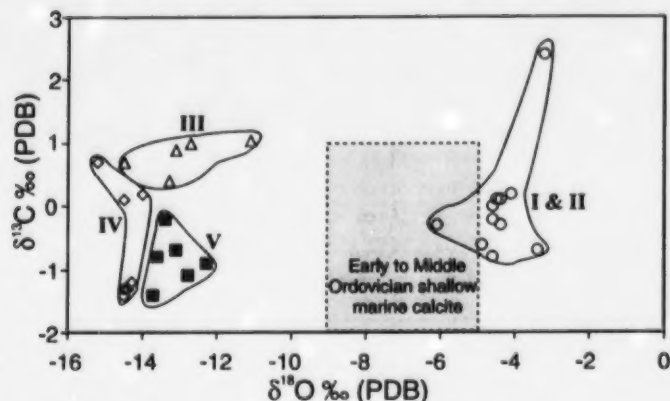
isopachous calcite; IV) bright-luminescent, blocky calcite; and V) dull-luminescent, blocky calcite. Although a paragenetic sequence from types I through V can be recognized locally, crosscutting relationships (Fig. 2) suggest that such a sequence could have been repeated many times (Lavoie and Cousineau, 1995; Lavoie, 1997). Therefore, various carbonate phases can be considered to be penecontemporaneous. The presence of carbonate sediments indicates that the ophicalcite units were formed at or near the ocean floor.

The various carbonate phases have been analyzed for O and C isotopes (Lavoie and Cousineau, 1995; Lavoie, 1997). Because the O and C isotope data will be used in combination with fluid-inclusion data in this study, they are summarized in Figure 3 and briefly discussed below. The  $\delta^{13}\text{C}$  values of all the carbonate types fall in the range of Early to Middle Ordovician shallow-marine calcite (Qing and Veizer, 1994), and were used as an indication that the parent fluids were mainly derived from ocean water (Lavoie and Cousineau, 1995). The gap in  $\delta^{18}\text{O}$  between types I–II (–6.1 to –3.2‰) and III–V (–15.2 to –11.1‰) was interpreted to reflect a difference in precipitating temperature, i.e. types I–II were precipitated at ambient seafloor temperature, and types III–V



**Figure 2.** A generalized sketch showing crosscutting relationships between various carbonate phases in the ophicalcite units from southern Quebec Appalachians, based on the data of Lavoie and Cousineau (1995) and Lavoie (1997).





**Figure 3.**

A  $\delta^{18}\text{O} - \delta^{13}\text{C}$  diagram summarizing the stable isotope data of the various carbonate phases in the ophicalcite units from southern Quebec Appalachians (data from Lavoie and Cousineau, 1955; Lavoie, 1997). The ranges of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  of Early to Middle Ordovician shallow marine calcite (the shaded box) are from Qing and Veizer (1994). PDB = Peedee belemnites

were precipitated from hydrothermal fluids (Lavoie and Cousineau, 1995). If the two groups are assumed to have precipitated from fluids of the same isotopic composition, the gap in  $\delta^{18}\text{O}$  between types I–II and types III–V ( $\sim 10\text{‰}$ , see Fig. 3) corresponds to a difference in temperature of  $73^\circ\text{C}$  (assuming  $\delta^{18}\text{O}_{\text{fluid}} = 0\text{‰}$ , i.e. similar to modern seawater) or  $49^\circ\text{C}$  (assuming  $\delta^{18}\text{O}_{\text{fluid}} = -7\text{‰}$ , i.e. Ordovician seawater significantly depleted in  $^{18}\text{O}$ , as derived from data summarized in Qing and Veizer (1994)), using the equation of Friedman and O'Neil (1977). This gap also serves as an indication that the ophicalcite units were not subject to oxygen isotope re-equilibrium during later regional low-grade metamorphism (Lavoie and Cousineau, 1995). The difference in  $\delta^{18}\text{O}$  between types I–II and Early–Middle Ordovician shallow-marine calcite (shaded box in Fig. 3) was interpreted to indicate that the sedimentary calcite was precipitated from relatively cold, deep ocean water (Lavoie, 1997). This difference in  $\delta^{18}\text{O}$  ( $\sim 3\text{‰}$ ) corresponds to a difference in temperature of  $17^\circ\text{C}$  (assuming  $\delta^{18}\text{O}_{\text{sw}} = 0\text{‰}$ ) or  $11^\circ\text{C}$  (assuming  $\delta^{18}\text{O}_{\text{sw}} = -7\text{‰}$ ), using the equation of Friedman and O'Neil (1977).

## FLUID-INCLUSION MICROTHERMOMETRY

### Methods

Six samples that have been previously studied for O and C isotopes were examined for fluid inclusions. Workable fluid inclusions were only found in cements IV and V. Fluid-inclusion microthermometric measurements were carried out using a United States Geological Survey Heating-Freezing Stage made by Fluid Inc. The sizes of most of the studied inclusions are in the range of  $4\text{--}10\text{ }\mu\text{m}$ , requiring a routine use of the cycling technique for measurement of both homogenization temperature ( $T_h$ ) and final ice-melting temperature ( $T_{m\text{-ice}}$ ) (see Goldstein and Reynolds, 1994). For fluid inclusions that contain only liquid at room temperature, a bubble was artificially created by overheating in order to measure the final ice-melting temperature. Homogenization temperature and final ice-melting temperature were

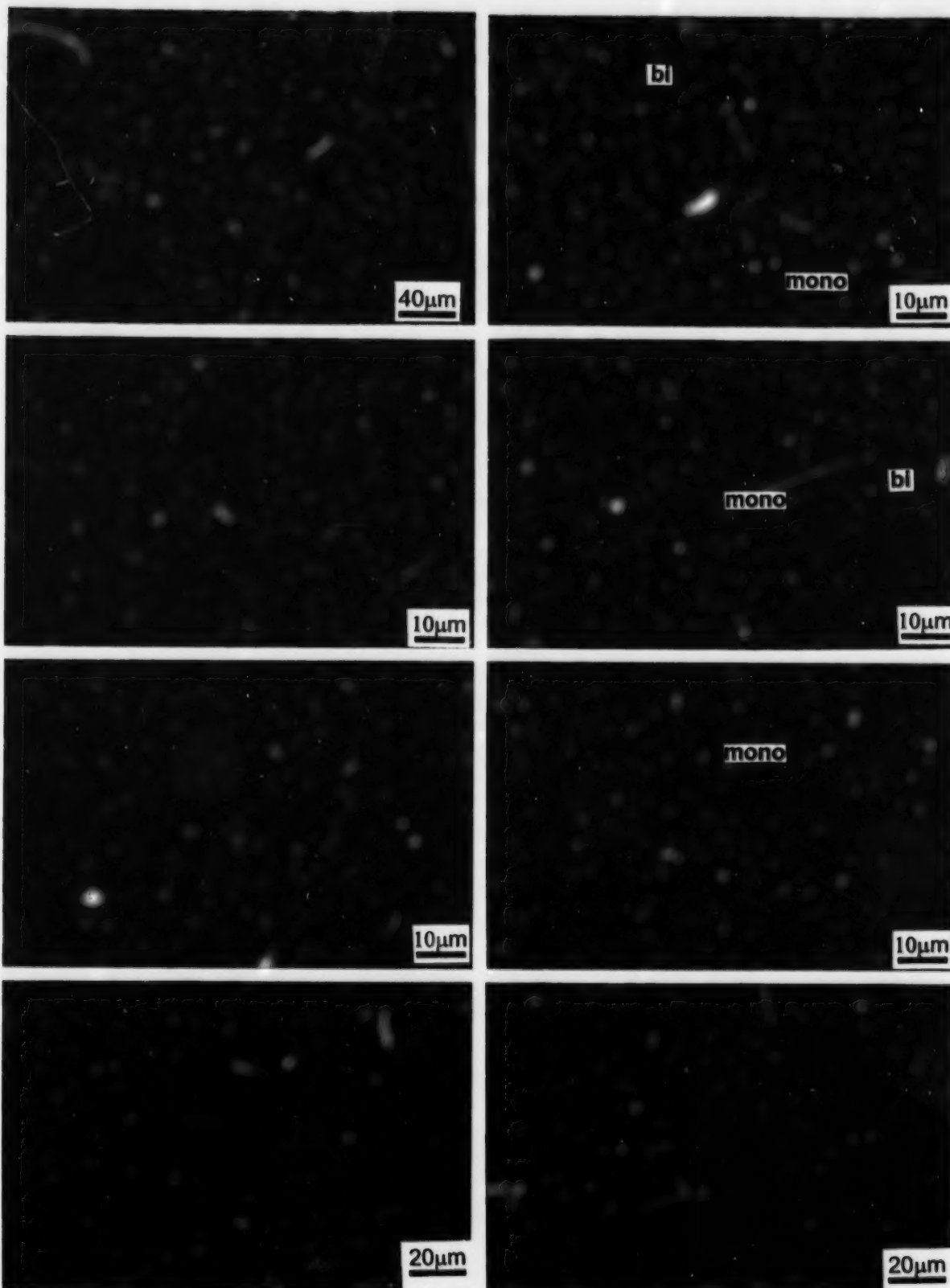
measured with a precision of  $\pm 1^\circ\text{C}$  and  $\pm 0.2^\circ\text{C}$ , respectively. The final identification of the carbonate phases was made using cathodoluminescence after the microthermometric runs.

### Fluid-inclusion petrography

Crystals of type IV calcite typically contain numerous fluid inclusions that are randomly distributed (Fig. 4A, B) or relatively isolated (Fig. 4C, D). Type V calcite is relatively clean, and contains isolated (Fig. 4E) or randomly distributed (scattered) fluid inclusions or clusters of inclusions (Fig. 4F). Fluid inclusions distributed along microfractures terminating at or crosscutting crystal boundaries are common in both type IV and type V calcite (Fig. 4G, H). Fluid inclusions that are randomly distributed, isolated, or in cluster without obvious fracture control are referred to as type A, and those distributed along microfractures are referred to as type B. Type A fluid inclusions are probably primary or pseudosecondary, but their origins remain indeterminate because no unambiguous relationships with the growth of crystals can be identified. Type B fluid inclusions are secondary in origin. In terms of phase assemblage at room temperature, the fluid inclusions in calcite IV and V can be divided into a monophasic (liquid-only) and a biphasic (liquid+vapor) type. Both biphasic and

**Figure 4.**

Photomicrographs showing modes of occurrence of fluid inclusions in calcite IV and V. **A)** Randomly distributed fluid inclusions in calcite IV. **B)** Enlargement of a part of A, showing 'co-existence' of biphasic and monophasic fluid inclusions. **C)** A relatively isolated fluid inclusion in calcite IV. **D)** 'Co-existence' of a monophasic fluid inclusion (relatively large) and a cluster of biphasic fluid inclusions (relatively small) in calcite IV. **E)** An isolated fluid inclusion in calcite V. **F)** A cluster of monophasic fluid inclusions in calcite V. **G)** Biphasic fluid inclusions distributed along a healed fracture in calcite V. **H)** Monophasic fluid inclusions distributed along a healed fracture in calcite V.



**Table 1.** Fluid-inclusion microthermometric data of Ordovician opicalcite units from southern Quebec.

Sample	Host*	Occurrence**	Size (µm)	Tm-ice(°C)		Salinity (wt% NaCl equiv.)		Th (°C)***		
				Range	Mean (n)	Range	Mean (n)	Range	Mean (n)	
OPE-1	IV	R	4-7	-3.4 to -4.2	-3.8 (4)	5.5-6.7	6.2 (4)	142.6-170.1	162.0 (5)	
		R	6-7	-	-	-	-	120.6-125.6	123.1 (2)	
		R	4-5	-3.4	-3.4 (1)	5.5	5.5 (1)	160.9-186.2	173.1 (3)	
		R	4-6	-3.4	-3.4 (1)	5.5	5.5 (1)	124.4-152.3	135.6 (4)	
		R	5-8	-2.9	-2.9 (1)	4.8	4.8 (1)	103.6-113.2	108.1 (3)	
		R	4-7	-3.8	-3.8 (1)	6.1	6.1 (1)	120.3-132.1	126.5 (3)	
		R	4-8	-2.9	-2.9 (1)	4.8	4.8 (1)	133.2-135.8	134.5 (2)	
		R	4-5	-4.1	-4.1 (1)	6.6	6.6 (1)	138.2-140.1	139.2 (2)	
		R	5-6	-3.9	-3.9 (1)	6.3	6.3 (1)	127.8-139.5	132.2 (3)	
		R	7-12	-2.4 to -3.2	-2.8 (4)	4.0-5.2	4.7 (4)	114.8-137.8	128.8 (5)	
OPE-4	IV	R	6-12	-4.0	-4.0 (1)	6.4	6.4 (1)	117.8-125.2	121.5 (2)	
		R	5-8	-2.5 to -2.5	-2.5 (2)	4.2-4.2	4.2 (2)	124.1-127.0	125.6 (2)	
		R	10	-	-	-	105.1	105.1 (1)		
		R	12	-4.9	-4.9 (1)	7.7	7.7 (1)	L	L	
		R	7	-3.4	-3.4 (1)	5.5	5.5 (1)	L	L	
	V	F	10	-4.1	-4.1 (1)	6.6	6.6 (1)	L	L	
		C	5-8	-4.0 to -4.7	-4.4 (2)	6.4-7.4	6.9 (2)	107.2-116.2	110.9 (3)	
		R	4-9	-4.7 to -5.0	-4.9 (2)	7.4-7.9	7.7 (2)	75.0-109.2	97.7 (15)	
		R	7	-4.7	-4.7 (1)	7.4	7.4 (1)	118.6	118.6 (1)	
		I	10	-4.3	-4.3 (1)	6.9	6.9 (1)	L	L	
OPE-12	IV	R	10	-5.2	-5.2 (1)	8.1	8.1 (1)	L	L	
		C	18	-4.4	-4.4 (1)	7.0	7.0 (1)	L	L	
		F	5-8	-2.6 to -3.3	-3.0 (3)	4.3-5.4	4.9 (3)	115.6-120.3	116.2 (6)	
		F	7-12	-4.5 to -5.7	-5.2 (3)	7.2-8.8	8.1 (3)	L	L	
		F	8-11	-3.0 to -3.1	-3.1 (2)	4.9-5.1	5.0 (2)	L	L	
		F	15	-4.7	-4.7 (1)	7.4	7.4 (1)	L	L	
		R	7-12	-2.5 to -3.1	-2.9 (3)	4.2-5.1	4.7 (3)	130.5-144.8	136.8 (5)	
		R	5-7	-	-	-	-	124.9-127.5	126.2 (2)	
		R	4-6	-4.1 to -4.2	-4.2 (2)	6.6-6.7	6.7 (2)	133.6-163.7	151.2 (5)	
		R	4-6	-3.1	-3.1 (1)	5.1	5.1 (1)	114.8-116.2	115.5 (2)	
OPE-18	IV	R	4-9	-2.9 to -3.7	-3.2 (3)	4.8-6.0	5.2 (3)	132.9-148.6	137.1 (5)	
		V	I	6	-6.1	-6.1 (1)	9.4	9.4 (1)	93.8	93.8 (1)
			C	3-4	-5.2	-5.2 (1)	8.1	8.1 (1)	87.3-96.6	92.0 (2)
			R	4-8	-	-	-	-	85.6-103.0	94.3 (2)
			C	5-14	-4.4	-4.4 (1)	7.0	7.0 (1)	121.2-139.8	130.5 (2)
			I	5	-	-	-	-	94.3	94.3 (1)
		I	10	-2.6	-2.6 (1)	4.3	4.3 (1)	150.7	150.7 (1)	
		R	6-7	-3.7	-3.7 (1)	6.0	6.0 (1)	126.0-144.6	132.3 (4)	
		R	6-10	-2.7 to 3.4	-3.1 (2)	4.5-5.5	5.0 (2)	107.0-121.5	113.9 (3)	
		R	4-5	-3.8 to 4.0	-3.9 (2)	6.1-6.4	6.3 (2)	98.5-105.7	101.9 (4)	
OPE-21	IV	R	5-8	-2.6	-2.6 (1)	4.3	4.3 (1)	87.0-121.5	104.5 (5)	
		R	4-7	-4.5	-4.5 (1)	7.2	7.2 (1)	93.8-109.7	101.8 (2)	
		R	4-8	-4.1 to 4.6	-4.4 (3)	6.6-7.3	7.0 (3)	103.4-119.7	110.7 (5)	
		R	5-7	-4.3 to 4.4	-4.4 (2)	6.9-7.0	7.0 (2)	82.4-109.9	97.3 (6)	
		V	R	10-15	-5.6 to 5.8	-5.7 (2)	8.7-9.0	8.9 (2)	121.4-140.7	126.8 (5)
			R	8-9	-6.3	-6.3 (1)	9.6	9.6 (1)	95.6-103.6	98.7 (3)
			R	10-14	-3.1 to -4.3	-3.7 (3)	5.1-6.9	6.0 (3)	133.3-169.7	146.0 (3)
			C	6-12	-4.5 to -4.5	-4.5 (2)	7.2-7.2	7.2 (2)	105.2-118.3	110.2 (7)
			C	5-7	-6.4	-6.4 (1)	9.7	9.7 (1)	90.2-92.3	91.2 (3)
		OPE-23	V	I	6	-6.6	-6.6 (1)	10.0	10.0 (1)	84.6
I	7			-4.7	-4.7 (1)	7.4	7.4 (1)	103.3	103.3 (1)	
R	4-8			-3.4 to 3.7	-3.6 (3)	5.5-6.0	5.8 (3)	112.7-126.1	119.0 (7)	
R	5-8			-2.9 to -2.9	-2.9 (2)	4.8-4.8	4.8 (2)	100.7-119.0	110.6 (3)	
C	C			4-8	-2.5 to -2.5	-2.5 (2)	4.2-4.2	4.2 (2)	101.1-116.4	107.4 (3)
	I			7	-2.6	-2.6 (1)	4.3	4.3 (1)	108.0	108.0 (1)
	I			5	-2.4	-2.4 (1)	4.0	4.0 (1)	102.1	102.1 (1)
	C			4-9	-2.4 to 2.7	-2.6 (2)	4.0-4.5	4.3 (2)	103.3-120.5	113.4 (8)
	I			9	-2.6	-2.6 (1)	4.3	4.3 (1)	118.5	118.5 (1)
C	5-15			2.2-3.4	-2.6 (5)	3.7-5.5	4.3 (5)	114.1-115.9	114.9 (10)	
C	6-7	-	-	-	-	122.1-124.6	123.4 (2)			
C	6-9	-2.3 to -2.3	-2.3 (2)	3.9-3.9	3.9 (2)	109.1-121.9	115.8 (3)			
C	10-12	-2.3	-2.3 (1)	3.9	3.9 (1)	125.3-129.3	127.0 (3)			
C	8-16	-2.1 to -2.4	-2.3 (3)	3.5-4.0	3.7 (3)	115.6-138.8	126.3 (4)			

\*IV - luminescent under calcite; V - dull calcite.

\*\*R - randomly distributed; C - cluster; I - isolated; F - fractures cutting or terminating at crystal boundaries.

\*\*\*L - liquid-only inclusion



monophase inclusions occur as type A (Fig. 4A–F) and type B (Fig. 4G, H). Therefore, there are four combinations of occurrence of fluid inclusions, type A biphasic, type A monophase, type B biphasic, and type B monophase.

### Microthermometric results

Fluid inclusions of all types described above were measured for homogenization temperature ( $T_h$ ) (except for monophase fluid inclusions) and final ice-melting temperature ( $T_{m-ice}$ ). The results are listed in Table 1. Most data were obtained from type A biphasic fluid inclusions. The measurement of  $T_{m-ice}$  of monophase fluid inclusions requires the presence of a vapor bubble, which is artificially created by heating the inclusions to 300–420°C and then cooling back to room temperature. Many monophase fluid inclusions remain the same after the overheating treatment. Monophase fluid inclusions (both types A and B) and type B fluid inclusion were studied in one sample (OPE-4). The  $T_h$  and  $T_{m-ice}$  data are plotted in Figure 5, where each point represents the average values of individual group (e.g. an isolated inclusion, a cluster of inclusions, and fluid inclusions randomly distributed in a crystal).

The overall range of  $T_{m-ice}$  values is from –6.6°C to –2.3°C, corresponding to salinities of 3.7–10.0 wt % NaCl equivalent according to the equation of Oakes et al. (1990) with the compositional system being approximated by H<sub>2</sub>O–NaCl. The upper limits of the  $T_{m-ice}$  values are close to, but nevertheless slightly lower than that of modern seawater (about –1.9°C) (Fig. 5). There is no systematic difference in  $T_{m-ice}$  between fluid inclusions hosted by cements IV (–2.5° to –4.5°C) and V (–2.3°C to –6.6°C), although  $T_{m-ice}$  values of fluid inclusions in cement V appear to be more variable (Fig. 5). The  $T_{m-ice}$  values of monophase inclusions, either type A or type B, fall in a relatively small interval (–3.1°C to –5.2°C) within the range of biphasic inclusions (Fig. 5).

The overall range of homogenization temperatures ( $T_h$ ) of biphasic fluid inclusions is from 85–173°C. The  $T_h$  values from cement IV (97–173°C) are slightly higher than, but largely overlap with those from cement V (85–151°C) (Fig. 5). The  $T_h$  values within clusters of fluid inclusions or randomly distributed fluid inclusions in individual crystals are relatively convergent. The difference in  $T_h$  is generally

less than 20°C (Table 1), but it may be higher than 30°C in the case of randomly distributed inclusions. The  $T_h$  values of monophase fluid inclusions are unknown (lack of a vapor bubble at room temperature is most likely due to metastability), but they are possibly less than or equal to 50°.

### DISCUSSION AND CONCLUSIONS

The relationship between type A biphasic and type A monophase fluid inclusions merits special attention because these two types of fluid inclusions may reflect two very different thermal conditions. In many cases, type A biphasic and type A monophase inclusions belong to different groups (e.g. isolated inclusions or clusters of inclusions; Fig. 4E, F). In other cases, especially when fluid inclusions are randomly and densely distributed, biphasic and monophase inclusions cannot be separated into distinct groups (Fig. 4B, D). The apparent co-existence of biphasic and monophase fluid inclusions does not appear to be caused by necking down of originally biphasic inclusions. The convergence of  $T_h$  values of biphasic fluid inclusions in individual crystals and the fact that in a given crystal, big inclusions, which are more prone to stretching, are monophase whereas small inclusions are biphasic (e.g. Fig. 4D), argue against the possibility that the biphasic fluid inclusions resulted from stretching of originally monophase fluid inclusions. A possible interpretation of the co-existence of biphasic and monophase fluid inclusions is that these inclusions belong to different generations. We believe that either monophase or biphasic fluid inclusions of type A are primary in origin, but remain indeterminate as to which one is primary, because we have not found an unequivocal relationship between fluid-inclusion distribution and crystal growth (Goldstein and Reynolds, 1994).

Despite the uncertainties about the origins of fluid inclusions, the microthermometric data presented above may be accommodated in a seafloor hydrothermal system. We have shown earlier that the difference in  $\delta^{18}\text{O}$  between types I–II and III–V (~10‰, see Fig. 3) may correspond to a difference in temperature of 49°C or 73°C, which means that there was a significant change in thermal conditions during the formation of the ophtalcite units. Thus, if the type A biphasic fluid inclusions in calcite types IV–V are primary, then the type A

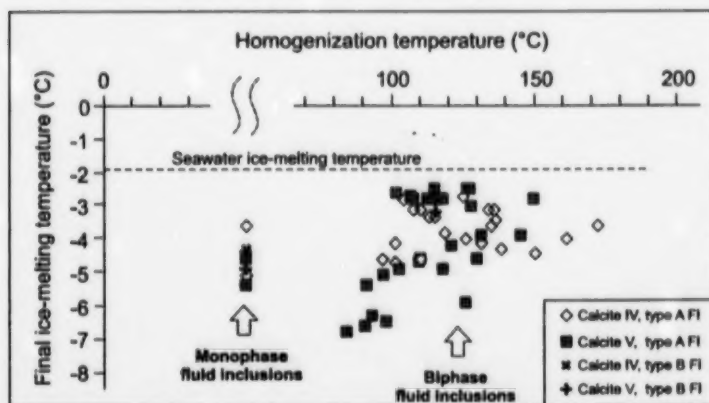


Figure 5.

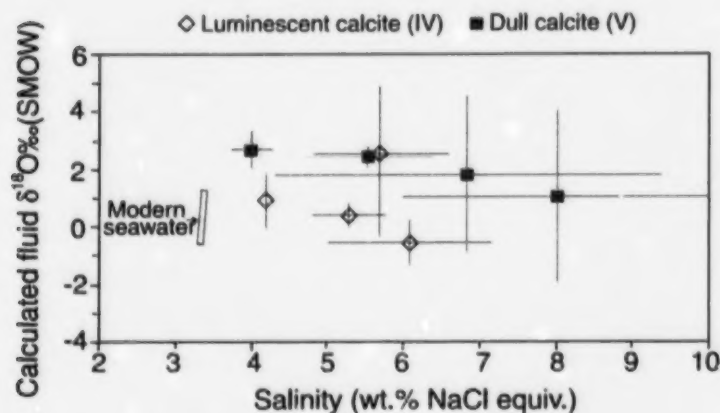
A diagram showing the relationship between fluid-inclusion homogenization temperature and final ice-melting temperature. Note the upper limits of the  $T_{m-ice}$  values are close to, but nevertheless slightly lower than that of modern seawater (~ –1.9°C). The  $T_h$  of monophase fluid inclusions are assumed to be around 50°C.

**Table 2.** Summary of fluid-inclusion data and calculation of oxygen isotopes of parent fluids.

Sample #	Calcite phase	Type-A biphasic fluid inclusions		Calcite O isotopes	Calculated fluid O isotopes	
		$T_h$ (°C)	Salinity (wt.% NaCl equiv.)	$\delta^{18}O_{\text{calc}}$ (PDB)*	$\delta^{18}O_{\text{fluid}}$ (SMOW) (from biphasic FI)	$\delta^{18}O_{\text{fluid}}$ (SMOW) (from monophasic FI)**
OPE-1	IV	108.1–173.1 (n=9)	4.8–6.6 (n=8)	-14.5	-0.3 to 4.9	-7.8
	V	121.5–128.8 (n=2)	4.7–6.4 (n=2)	-13.4	2.1 to 2.8	-6.6
OPE-4	IV	105.1–125.6 (n=2)	4.2 (n=1)	-14.0	-0.1 to 1.9	-7.3
	V	97.7–118.6 (n=3)	6.9–7.7 (n=3)			
OPE-12	IV	115.5–151.2 (n=5)	4.7–6.7 (n=4)			
	V	92.0–150.7 (7)	4.3–9.4 (n=5)	-13.4	-0.9 to 4.5	-6.6
OPE-18	IV	97.3–113.9 (n=6)	5.0–7.2 (n=6)	-14.5	-1.4 to 0.3	-7.8
	V	84.6–146.0 (n=7)	6.0–10.0 (n=7)	-13.6	-1.9 to 4.0	-6.8
OPE-21	IV	110.6–119.0 (n=2)	4.8–5.8 (n=2)	-14.5	0.0 to 0.8	-7.8
	V	102.1–108.0 (n=3)	4.0–4.3 (n=3)			
OPE-23	V	113.4–128.3 (n=7)	3.7–4.3 (n=6)	-12.8	2.0 to 3.4	-6.0

\* Isotope data of calcite are from Lavoie and Coussineau (1995).

\*\* A temperature of 50°C is assumed for monophasic fluid inclusions.

**Figure 6.**

A diagram showing the relationship between fluid-inclusion salinity and  $\delta^{18}O_{\text{fluid}}$  calculated from  $T_h$  and  $\delta^{18}O_{\text{calc}}$  (data from Table 2). The horizontal and vertical bars represent the range of variation. The range of modern seawater is from Veizer (1983).

monophasic fluid inclusions are secondary and may represent fluids that precipitated calcite types I–II. Conversely, if the type A monophasic fluid inclusions in calcite types IV–V are primary, then calcite types I–II must have been precipitated in a cold environment, and the type A biphasic fluid inclusions in calcite types IV–V probably represent secondary fluid inclusions entrapped during later regional metamorphism. The implications of these two possibilities on the oxygen isotope composition of the parent fluids are discussed below.

### Case 1

If type A biphasic fluid inclusions are assumed to be primary, the possible range of  $\delta^{18}O$  of the parent fluids may be calculated from the  $\delta^{18}O$  value of the calcite and the range of homogenization temperatures, using the equation of Friedman and O'Neil (1977). No pressure correction is attempted considering the uncertainties of fluid-inclusion origins. The overall range of calculated  $\delta^{18}O_{\text{fluid}}$  is from  $-1.9\text{‰}$  to  $+4.9\text{‰}$  (Table 2). In an attempt to see how the calculated  $\delta^{18}O_{\text{fluid}}$  values may be related to the oxygen isotopes of coeval

seawater, we plot fluid-inclusion salinity values versus the  $\delta^{18}O_{\text{fluid}}$  values (Fig. 6). It is thought that if the parent fluids of the calcite cements originated from seawater, we might see a correlation trend between salinity and  $\delta^{18}O_{\text{fluid}}$  that can be traced back to the original composition of seawater. As shown in Figure 6, a poorly defined negative correlation between  $\delta^{18}O_{\text{fluid}}$  and salinity is observed. It might be inferred from this trend that the initial  $\delta^{18}O$  value of the seawater was around  $+2\text{‰}$  to  $+3\text{‰}$  SMOW, which is slightly higher than modern seawater.

### Case 2

Conversely, if the type A monophasic fluid inclusions are assumed to be primary, then the calculated  $\delta^{18}O_{\text{fluid}}$  values are very different from that of modern seawater. Assuming a temperature of 50°C for the monophasic fluid inclusions,  $\delta^{18}O_{\text{fluid}}$  values are calculated to be from  $-7.8\text{‰}$  to  $-6.6\text{‰}$  SMOW (Table 2), which is significantly lower than that of modern seawater.

In summary, the results of the present study agree with the previous hypothesis that the calcite cements in the ophicalcite units were precipitated from heated ocean water (Lavoie and Cousineau, 1995). However, uncertainties about the oxygen isotope composition of the parent fluids arise from difficulties in unambiguously determining the origins of two sets of fluid inclusions. It is hoped that the results of the present study will stimulate further investigations in this direction, which will contribute to a better understanding of the isotopic composition of ancient ocean water (Muehlenbachs, 1998; Veizer et al., 1998).

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